

Steroid Estrogens, Nonylphenol Ethoxylate Metabolites, and Other Wastewater Contaminants in Groundwater Affected by a Residential Septic System on Cape Cod, MA

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Septic systems serve approximately 25% of U.S. households and may be an important source of estrogenic and other organic wastewater contaminants (OWC) to groundwater. We monitored several estrogenic OWC, including nonylphenol (NP), nonylphenol mono- and diethoxycarboxylates (NP1EC and NP2EC), the steroid hormones 17 β -estradiol (E2), estrone (E1) and their glucuronide and sulfate conjugates, and other OWC such as methylene blue active substances (MBAS), caffeine and its degradation product paraxanthine, and two fluorescent whitening agents in a residential septic system and in downgradient groundwater. E1 and E2 were present predominantly as free estrogens in groundwater, and near-source groundwater concentrations of all OWC were highest in the suboxic to anoxic portion of the wastewater plume, where concentrations of most OWC were similar to those observed in the septic tank on the same day. NP and NP2EC were up to 6- to 30-fold higher, and caffeine and paraxanthine were each 60-fold lower than septic tank concentrations, suggesting net production and removal, respectively, of these constituents. At the most shallow, oxic depth, concentrations of all OWC except for NP2EC were substantially lower than in the tank and in deeper wells. Yet boron, specific conductance, and the sum of nitrate- and ammonia-nitrogen were highest at this shallow depth, suggesting preferential losses of OWC along the more oxic flow lines. As far as 6.0 m downgradient, concentrations of many OWC were within a factor of 2 of near-source concentrations. The results suggest that there is the potential for migration of these OWC, which are unregulated and not routinely monitored, in groundwater.

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Introduction

Research on hormonally active and other organic wastewater contaminants (OWC), such as natural steroid hormones, constituents of personal care products and detergents, and excreted or unused pharmaceuticals, has focused on surface waters receiving point-source wastewater treatment plant (WWTP) discharges (1–7). Few studies have examined the infiltration of these classes of OWC into groundwater from on-site wastewater treatment, such as septic systems (8). On-site systems represent a substantial share of global wastewater handling, and septic systems may not treat waste as effectively as centralized WWTP due to poor placement, undetected failure, and anaerobic conditions that typically prevail in these systems. In regions with a high density of septic systems, discharge of OWC to groundwater that subsequently recharges surface waters could affect ecological health (8,9), and where groundwater is the primary or sole source of drinking water, human exposure to OWC may result. Therefore, it is important to understand the fate of these chemical classes in groundwater.

On Cape Cod, MA, greater than 85% of residential and commercial properties are serviced by septic systems that discharge wastewater effluent to a shallow, sandy aquifer that is the sole source of drinking water for the region (10). The Cape Cod aquifer has become increasingly impacted by wastewater contamination over the last 30 years (11), and its vulnerability to the migration of OWC has been documented (12–14). Several OWC have been identified in samples collected from private drinking water wells (14).

To understand the fate of estrogenic OWC introduced to groundwater from septic systems, we installed a series of sampling wells immediately downgradient from a septic system leachate pit that serves a multi-residential property on Cape Cod in order to monitor the distribution of selected estrogenic compounds, including 17 β -estradiol (E2), estrone (E1), and their respective water soluble glucuronide and sulfate conjugates; the latter being the primary form of the hormones excreted in human urine.

Other estrogenic OWC targeted in this analysis include the degradation products of nonylphenol ethoxylate (NPEO) surfactants, including nonylphenol (NP), nonylphenol mono- to triethoxylates (NP1-3EO), and nonylphenol mono- and diethoxycarboxylates (NP1EC and NP2EC). Earlier studies have highlighted these constituents as contributors to estrogenic activity in wastewaters (15).

In this paper, we evaluate the subsurface migration of OWC relative to several wastewater co-contaminants that traditionally have been used as indicators of wastewater impact. These constituents include nitrate- and ammonia-nitrogen (NO₃-N and NH₃-N); specific conductance; alkalinity; detergent components such as ethylenediaminetetraacetic acid (EDTA) (16), boron (12, 13, 16), and the fluorescent whitening agents (FWAs) 4,4-bis[(4-anilino-6-morpholino-1,3,5-triazin-2-yl)amino]stilbene-2, 2-disulfonate (DAS) and 4,4-bis(2-sulfostyryl)biphenyl (DSBP) (17–19); and caffeine and its metabolite paraxanthine (20, 21). Understanding the behavior and transport of estrogenic OWC relative to these wastewater indicators can improve our understanding of the migratory potential of the former in groundwater and may provide additional tools for identifying groundwater impacted by estrogenic contaminants.

Experimental Section

Site Characterization. The study site is located on Cape Cod, MA, a 440-km² area underlain by an unconfined aquifer

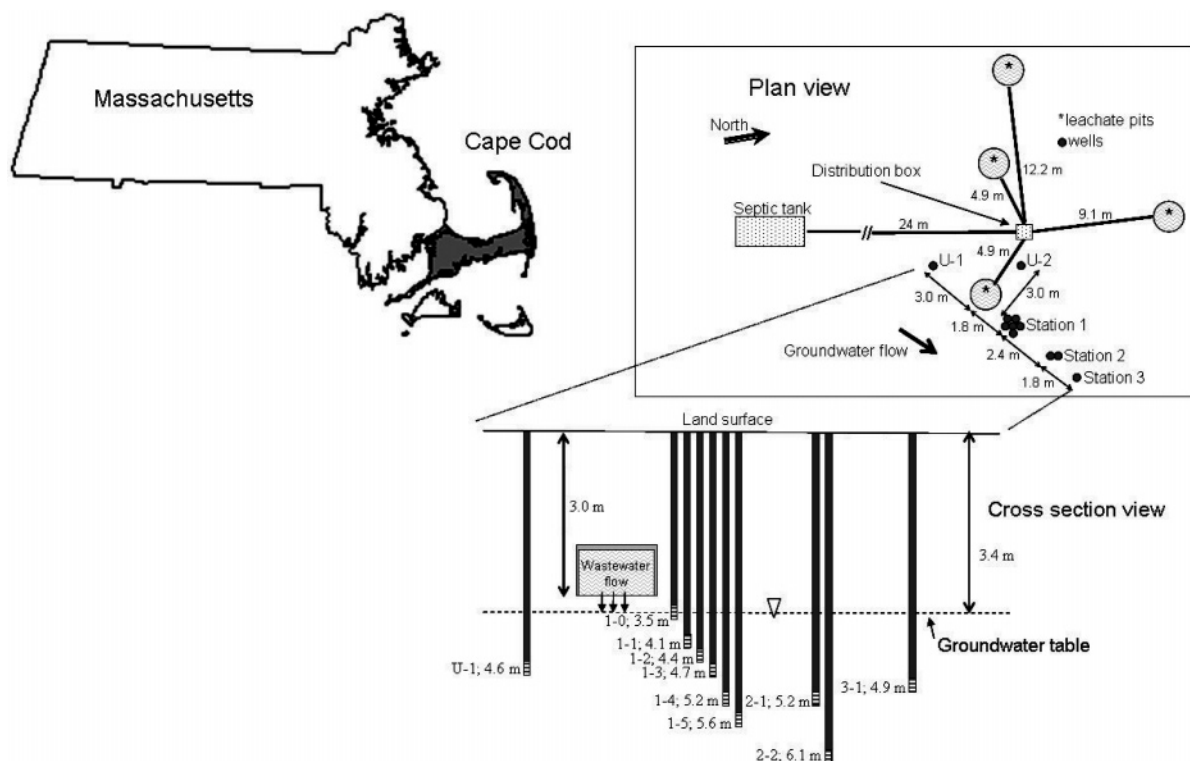


FIGURE 1. Map of Massachusetts with Cape Cod shaded and plan and cross section (insets) schematics of the field site, including position of the three well cluster stations downgradient of the leachate pit and the two upgradient wells U-1 and U-2 (U-2 not shown in cross section). The approximate groundwater flow direction is indicated in the plan view.

composed of glacial deposits of sand and gravel (10). The 2.3-acre property comprises a main house and four cottages served by a single septic tank (capacity of approximately 7600 L) installed in 1989 and from which wastewater is distributed to four leachate pits, each 1.8 m in diameter and 0.9 m in depth (Figure 1 plan view). The discharge points for these pits lie approximately 3.0 m below land surface (bls) and 0.4 m above the present water table (at approximately 3.4 m bls, Figure 1 cross section view).

Well Placement and Installation. The locations of the four leachate pits were identified using a map drafted at the time of the septic system installation; ground penetrating radar confirmed these locations. A single pit was chosen for this investigation, and three clusters of wells were installed downgradient of this pit in two phases (Table 1). The screened intervals of these wells span depths of 3.5–6.1 m bls at distances of 1.8 m (station 1), 4.2 m (station 2), and 6.0 m (station 3) from the center of the leach pit (Figure 1). Additional wells were subsequently placed (Table 1) either immediately or obliquely upgradient (U-1 and U-2; Figure 1) from the pit to determine if wastewater-impacted groundwater from any upgradient sources was intercepting the study site.

Monitoring wells were constructed of either 1.9- or 2.5-cm inside diameter hollow stainless steel drive points with 30 cm long screened intervals. These drive points were installed with a vibratory drill rig to minimize disruption of the surrounding aquifer sediments. At station 1, final screen depths were chosen to provide coverage of the vertical extent of the wastewater plume, determined from measurements of ammonia and nitrate nitrogen ($\text{NH}_3\text{-N}$ and $\text{NO}_3\text{-N}$, respectively), dissolved oxygen (DO), and methylene blue active substances (MBAS) (see the Analyses section below) analyzed in samples collected at discrete depths as a trial drive point was driven sequentially downward. A limited number of exploratory depths were selected for stations 2 and 3 in the same manner.

Sample Collection and Preservation. Groundwater was collected for analysis of selected OWC during three sampling events in July 2003, November 2003, and August 2004; the septic tank was sampled only during the November 2003 sampling event. Only E2, E1, and their conjugates were analyzed in the August 2004 samples, and conjugates were analyzed only in August 2004. Monitoring of general aqueous properties and constituents also occurred during these sampling events and in November 2004 as well. Samples were obtained using a peristaltic pump, and 0.6-cm inside diameter Teflon tubing inserted down each well to the screened interval.

Samples for OWC analysis were collected in 1-liter amber glass bottles pre-cleaned by heating at 450 °C, placed in-line upstream from the peristaltic pump, and filled from the bottom upward using a Teflon manifold. After displacing at least three bottle volumes, bottles were capped and placed on ice for overnight transport to the laboratory. Most samples for analysis of OWC were preserved immediately upon collection by acidifying to approximately pH 2 with H_2SO_4 with the exception of the hormones, which were acidified in the August 2004 sampling event only. Samples for determining general aqueous constituents were collected in 125-mL polyethylene bottles.

Analyses. Chemets (Chemetrics, Calverton, VA) were used to measure DO, $\text{NH}_3\text{-N}$, $\text{NO}_3\text{-N}$, Fe^{2+} , total Fe, total sulfide, and MBAS immediately upon collection. DO was likely overestimated because of brief atmospheric contact during the Chemet analyses. Boron was determined by ICP-MS in unfiltered water collected in polyethylene bottles and preserved with nitric acid. Specific conductance measurements and alkalinity titrations were performed in the laboratory on archived samples.

The methods for analysis of OWC are summarized here, and additional detail is provided in the Supporting Information. Filtration occurred within 24 h of sampling through 47 mm Gelman GF/C filters, followed by an addition of

TABLE 1. Aqueous Concentrations of Detergent Components

location ^a	screened interval depth (mbls) ^b	boron $\mu\text{g/L}^c$	EDTA $\mu\text{g/L}^c$	MBAS mg/L^c	DAS ng/L^c	DSBP ng/L^c	NP1EO–NP3EO $\mu\text{g/L}^c$	NP $\mu\text{g/L}^c$	NP1EC $\mu\text{g/L}^c$	NP2EC $\mu\text{g/L}^c$
septic tank ^d		216 \pm 8 ^e	— ^f	—	2040, 1670 ^g	6.5, 2.8 ^g	3.9, 4.8 ^g	16, 10 ^g	7.8, 8.2 ^g	1.6, 2.3 ^g
U-1 ^h	4.3–4.6	—	—	—	—	—	—	—	—	—
		—	—	—	—	—	—	—	—	—
		—	—	—	—	—	—	—	—	—
		—	—	<0.2	—	—	—	—	—	—
U-2 ^h	3.5–3.8	—	—	—	—	—	—	—	—	—
		—	—	—	—	—	—	—	—	—
		—	—	—	—	—	—	—	—	—
		—	—	<0.2	—	—	—	—	—	—
1-0 ⁱ	3.2–3.5	—	—	0.9	4180	27	4.1	20	2.5	—
		181	28	0.2	16	1.4	0.1	0.7	bdl ^k	10
		—	—	—	—	—	—	—	—	—
		—	—	1.5	—	—	—	—	—	—
1-1 ^j	3.8–4.1	—	—	—	—	—	—	—	—	—
		174	29	1.0	750	2.7	1.9	53	7.2	25
		—	—	3.0	—	—	—	—	—	—
		—	—	2.5	—	—	—	—	—	—
1-2 ^j	4.1–4.4	—	—	—	—	—	—	—	—	—
		160	29	2.5	370	0.7	5.0	38	6.0	46
		—	—	3.0	—	—	—	—	—	—
		—	—	2.0	—	—	—	—	—	—
1-3 ^j	4.4–4.7	—	—	—	—	—	—	—	—	—
		148	44.5	3.0	2100	15	1.8	28	9.7	44
		—	—	3.0	—	—	—	—	—	—
		—	—	—	—	—	—	—	—	—
1-4 ^j	4.9–5.2	—	—	—	—	—	—	—	—	—
		61	15.7	0.8	1010	3.7	4.8	84	28	68
		—	—	<0.2	—	—	—	—	—	—
		—	—	<0.2	—	—	—	—	—	—
1-5 ^j	5.3–5.6	—	—	—	—	—	—	—	—	—
		17	3.8	0.2	bdl	1.8	0.02	bdl	bdl	4.4
		—	—	<0.2	—	—	—	—	—	—
		—	—	<0.2	—	—	—	—	—	—
2-1 ^j	4.9–5.2	—	—	—	—	—	—	—	—	—
		118	—	2.0	1300	5.2	3.3	42	16	65
		—	—	3.0	—	—	—	—	—	—
		—	—	<0.2	—	—	—	—	—	—
2-2 ^j	5.8–6.1	—	—	—	—	—	—	—	—	—
		16	—	0.2	12	0.7	0.07	0.1	0.3	16
		—	—	<0.2	—	—	—	—	—	—
		—	—	<0.2	—	—	—	—	—	—
3-1 ^j	4.6–4.9	—	—	—	—	—	—	—	—	—
		167	—	1.5	1064, 990 ^g	0.5, 4.9 ^g	1.0, 1.7 ^g	31, 48 ^g	18, 35 ^g	32, 69 ^g
		—	—	3.0	—	—	—	—	—	—
		—	—	<0.2	—	—	—	—	—	—

^a Identifier indicates upgradient (U) or station (1,2,3) and well number (Figure 1 plan and cross section views). ^b mbls indicates the meters below land surface. ^c For each well and constituent, measurements are arranged vertically for the July 2003, November 2003, August 2004, and November 2004 sampling events. ^d Septic tank sampled in November 2003. ^e Average \pm 1 standard deviation of six collected samples. ^f "—" indicates not measured. ^g Individual measurements for two collected samples. ^h Installed in November 2004. ⁱ Installed in July 2003. ^j Installed in November 2003. ^k bdl indicates below detection limit.

isotopically labeled surrogate standards [¹³C-labeled caffeine, NP, NP1-3EO and deuterated EDTA, E1, E2, E1-3-glucuronide (E1-3G) and sulfate (E1-3S), and E2-3-glucuronide and sulfate (E2-3G and E2-3S, respectively)], then solid-phase extraction (SPE) extraction within 72 h of sampling. Analyses by high-pressure liquid chromatography–mass spectrometry (HPLC–MS) or, for EDTA, gas chromatography–mass spectrometry (GC–MS), relied upon the method of isotope dilution utilizing published approaches (22–26), which account for incomplete recoveries or matrix-induced effects on ionization during electrospray ionization (ESI)–MS.

The analysis of NP, NP1-3EO, and NP1-2EC by HPLC–ESI–MS in negative ionization mode was modified from Ferguson et al. (22) to include an HPLC solvent gradient that allowed separation of NP from NP1EC and NP2EC; all three were quantified from their relative response to ¹³C–NP. Paraxanthine was determined along with caffeine by the method of Cahill et al. (26). DAS and DSBP were analyzed

by HPLC with fluorescence detection using a modification of the method of Poiger et al. (27).

Results and Discussion

Septic Tank Concentrations of OWCs. Many of the OWC concentrations measured in the septic tank (November 2003) are in the range of concentrations reported in the literature for wastewater and septage. These include DAS (1670–2040 ng/L; Table 1) (17, 19), NP (10–16 $\mu\text{g/L}$; Table 1) (14, 15, 28), and NP1EC (7.8–8.2 $\mu\text{g/L}$; Table 1) (3, 14, 24). Concentrations of the steroid hormones E2 (16–19 ng/L; Table 2) and E1 (49–74 ng/L; Table 2) are similar to (7, 25, 29) or somewhat higher (1, 28, 30, 31) than the ranges reported in other studies.

Concentrations of caffeine (17 000–23 000 ng/L; Table 2) are most similar to those reported for WWTP influent and septage (21, 24, 32, 33), and they represent approximately 25% of the sum of paraxanthine (55 000–65 000 ng/L; Table

TABLE 2. Aqueous Concentrations of Pharmaceuticals and Estrogens

location ^a	depth (mbls) ^b	caffeine (ng/L) ^c	paraxanthine (ng/L) ^c	E2 (ng/L) ^c	E1 (ng/L) ^c	E1-3S (ng/L) ^{c,d}
septic tank ^e		22900, 17 300 ^f	65 100, 54 900 ^f	19, 16 ^f	74, 49 ^f	—
U-1	4.3–4.6	— ^g	—	—	—	—
		—	—	—	—	—
		—	—	—	—	—
U-2	3.5–3.8	—	—	—	—	—
		—	—	—	—	—
		—	—	—	—	—
1-0	3.2–3.5	1710	1730	45	120	—
		16	bdl ^h	0.2	0.4	—
		—	—	—	—	—
1-1	3.8–4.1	—	—	—	—	—
		68	180	9.8	55	—
		—	—	—	—	bdl
		—	—	—	—	—
1-2	4.1–4.4	—	—	—	—	—
		330	630	29	100	—
		—	—	—	—	1.0
		—	—	—	—	—
1-3	4.4–4.7	—	—	—	—	—
		300	720	17	100	—
		—	—	—	—	4.0
		—	—	—	—	—
1-4	4.9–5.2	—	—	—	—	—
		320	890	4.7	24	—
		—	—	—	—	—
		—	—	—	—	—
1-5	5.3–5.6	—	—	—	—	—
		bdl	bdl	bdl	bdl	—
		—	—	bdl	bdl	bdl
		—	—	—	—	—
2-1	4.9–5.2	—	—	—	—	—
		200	940	—	—	—
		—	—	10	30	1.1
		—	—	—	—	—
2-2	5.8–6.1	—	—	—	—	—
		bdl	bdl	bdl	bdl	—
		—	—	bdl	bdl	bdl
		—	—	—	—	—
3-1	4.6–4.9	—	—	—	—	—
		68, 12 ^f	1320, 1180 ^f	0.3, 0.3 ^f	21, 23 ^f	—
		—	—	3.0	20	1.2
		—	—	—	—	—

^a Identifier indicates upgradient (U) or station (1,2,3) and well number (Figure 1 plan and cross section views). ^b mbls indicates meters below land surface. ^c For each well and constituent, measurements are arranged vertically for the July 2003, November 2003, August 2004, and November 2004 sampling events. ^d E1-3G, E2-3S, and E2-3G were below detection levels (0.1 to 0.2 ng/L). ^e Septic tank sampled in November 2003. ^f Individual measurements for two collected samples. ^g "—" indicates not measured. ^h bdl indicates below detection limit.

2) and caffeine in the tank. This fraction is higher than the range of 0.5–10% cited as excreted in urine (34). Unconsumed caffeine-containing products disposed of in the wastewater stream and fecal excretion would elevate this percentage.

Concentrations of other compounds are substantially lower than those reported in wastewaters elsewhere. DSBP (2.8–6.5 ng/L; Table 1) is more than 1000-fold lower than the range reported for raw sewage and treated effluent (17, 19), possibly indicating the local use of detergent formulations not containing substantial DSBP. The combined sum of NP1EO to NP3EO (3.9–4.8 µg/L; Table 1) is up to 100-fold lower than that reported for NP1-2EO in septage and WWTP influent and effluent (14, 15); values for NP3EO were not reported in these studies. NP2EC (1.6–2.3 µg/L; Table 1) is 10–100-fold lower than that observed in WWTP effluent (3, 24), perhaps due to the anaerobic conditions in the septic tank.

Near-Source Plume Delineation and Geochemistry. Based on traditional indicators of wastewater, the plume emanating from the leachate pit has a wedge-shaped profile

at station 1. The highest concentrations of the sum of NH₃-N and NO₃-N (Figure 2a), specific conductance (Figure 2b), alkalinity (Figure 2c), and boron (Figure 2d) occur at the most shallow depth (Tables 1 and 3), suggesting that the plume remains close to the water table at this distance from the leachate pit and has not sunk appreciably due to density effects or recharge (35, 36).

The wastewater plume appears to be diluted by at least 20% upon mixing with ambient groundwater. This estimate considers the highest boron concentration measured in the wastewater-impacted groundwater (181 µg/L; Table 1) and assumes a two-component mixing system characterized by end member concentrations in the septic tank (216 µg/L; Table 1) and in background concentrations for groundwater (16–17 µg/L; Table 1) collected from wells 1-5 and 2-2 apparently screened below the plume.

The wastewater concentrations measured at station 1 do not appear to be influenced by other upgradient wastewater sources. The sum of NH₃-N and NO₃-N (<0.4 mg/L; Table 3) in each of the two upgradient wells (U-1 and U-2, Figure

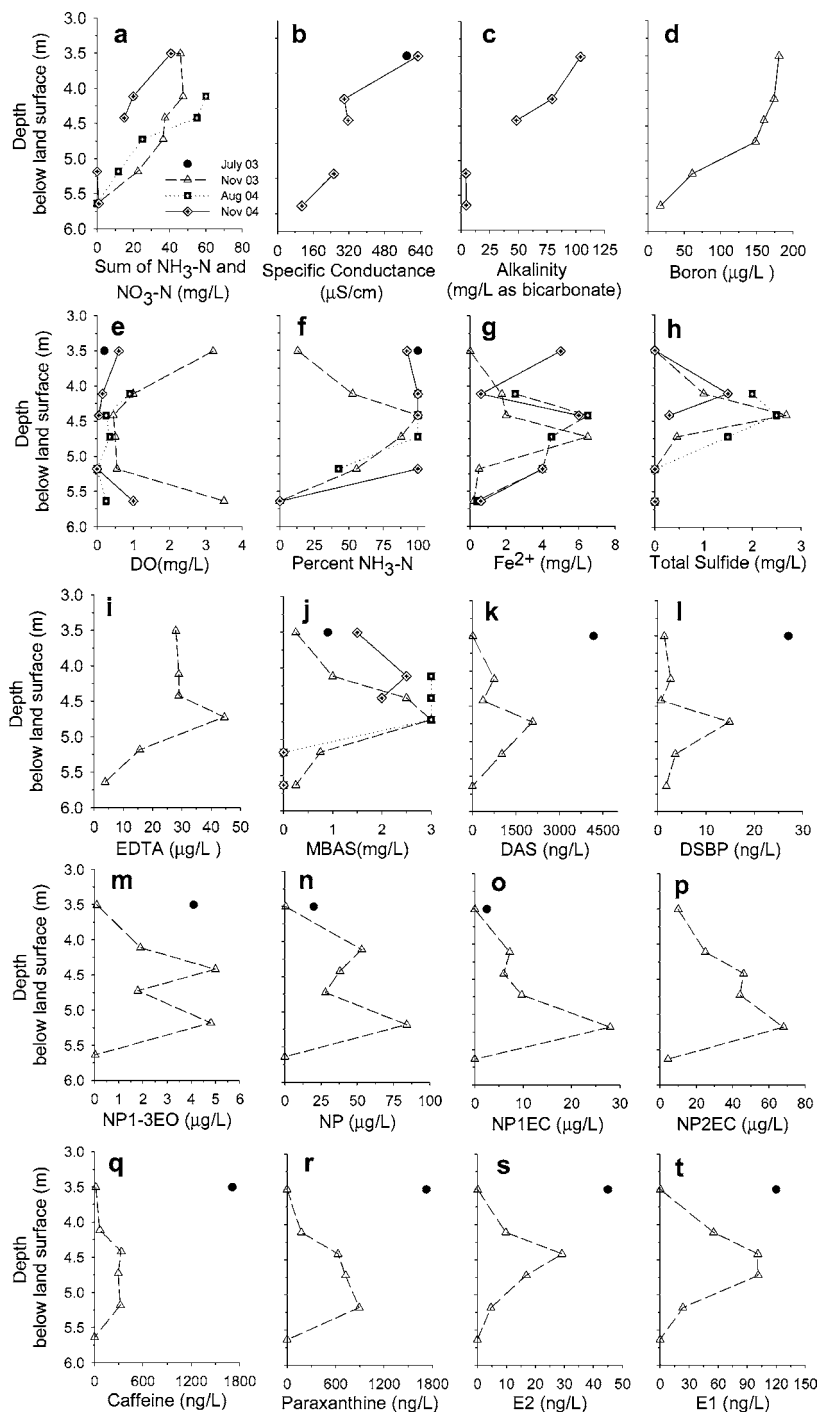


FIGURE 2. Depth profiles for aqueous constituents measured in station 1 wells, including (a) the sum of $\text{NH}_3\text{-N}$ and $\text{NO}_3\text{-N}$; (b) specific conductance; (c) alkalinity; (d) boron; (e) DO; total (f) percent $\text{NH}_3\text{-N}$ relative to sum of $\text{NO}_3\text{-N}$ and $\text{NH}_3\text{-N}$; (g) Fe^{2+} ; (h) sulfide; (i) EDTA; (j) MBAS; (k) DAS; (l) DSBP; (m) the sum of NP1-3EO; (n) NP; (o) NP1EC; (p) NP2EC; (q) caffeine; (r) paraxanthine; (s) E2; and (t) E1. Constituents were measured on one or more of the sampling dates July 2003 (●), November 2003 (△), August 2004 (□), and November 2004 (diamond with +).

1) was up to 100-fold lower than at similar depths at station 1.

Oxygenation conditions in the upper portion of the plume (wells 1-0 and 1-1; Table 3) alternated between sub-oxic/anoxic (July 2003, August 2004 and November 2004) to oxic (November 2003), but the core of the plume (wells 1-2, 1-3 and 1-4) was consistently sub-oxic/anoxic. For example, low DO (Figure 2e), elevated $\text{NH}_3\text{-N}$ (as a percent of the sum of $\text{NH}_3\text{-N}$ and $\text{NO}_3\text{-N}$; Figure 2f), Fe^{2+} (Figure 2g) and total sulfide (Figure 2h) occurred at depths of 4.1–5.2 m (wells 1-1 to 1-4; Table 3). The high proportion of $\text{NH}_3\text{-N}$ is likely due

to ammonification of organic matter and the absence of nitrification in the wastewater rather than to loss of $\text{NO}_3\text{-N}$ via denitrification, as suggested by low denitrification rates measured in another wastewater plume on Cape Cod (36).

Near-Source Vertical Profiles of OWC. The OWC profiles measured at station 1 in November 2003 differ dramatically from the wedge-shaped profiles exhibited by the sum of $\text{NH}_3\text{-N}$ and $\text{NO}_3\text{-N}$ and boron measured on the same day, which had maximum concentrations at the shallowest depth (Figure 2a and d, respectively). In contrast, the highest concentrations of EDTA, MBAS, DAS, DSBP, NP1-3EO, NP,

TABLE 3. General Aqueous Properties and Constituents

location ^a	screened Interval Depth mbls ^b	specific conductance $\mu\text{S}/\text{cm}^c$	DO mg/L ^c	NH ₃ -N mg/L ^c	NO ₃ -N mg/L ^c	Fe ²⁺ mg/L ^c	Fe _{total} mg/L ^c	total sulfide mg/L ^c	alkalinity mg/L as HCO ₃ ^{-c}
U-1	4.3–4.6	— ^d	—	—	—	—	—	—	—
		—	—	—	—	—	—	—	—
		—	—	—	—	—	—	—	—
U-2	3.5–3.8	117	0.2	<0.1	<0.1	2.0	2.0	0.2	5.4
		—	—	—	—	—	—	—	—
		—	—	—	—	—	—	—	—
		—	—	—	—	—	—	—	—
1-0	3.2–3.5	83	4.5	<0.1	0.3	1.5	1.5	<0.1	1.7
		580	0.2	45	<0.1	—	—	—	—
		—	3.2	6.0	40	<0.1	<0.1	<0.1	—
		—	—	—	—	—	—	—	—
1-1	3.8–4.1	630	0.6	37.5	3.2	4.5	5.0	<0.1	104
		—	—	—	—	—	—	—	—
		—	1.0	25	22	1.8	1.8	1.0	—
		—	0.9	60	<0.1	2.5	2.5	2.0	—
1-2	4.1–4.4	300	0.2	20	<0.1	0.6	0.7	1.5	79
		—	—	—	—	—	—	—	—
		—	0.4	38	<0.1	2.0	2.8	2.7	—
		—	0.2	55	<0.1	6.5	7.5	2.5	—
1-3	4.4–4.7	317	0.1	15	<0.1	6.0	6.5	0.3	48
		—	—	—	—	—	—	—	—
		—	0.5	32	4.5	6.5	7.0	0.4	—
		—	0.4	25	<0.1	4.5	9.0	1.5	—
		—	—	—	—	—	—	—	—
1-4	4.9–5.2	—	—	—	—	—	—	—	—
		—	0.6	13	10	0.5	0.7	<0.1	—
		—	<0.05	5.0	6.8	4.0	4.0	<0.1	—
1-5	5.3–5.6	253	<0.05	0.1	<0.1	4.0	4.5	<0.1	4.5
		—	—	—	—	—	—	—	—
		—	3.5	<0.1	0.2	0.2	0.2	<0.1	—
		—	0.2	<0.1	<0.1	0.4	0.4	<0.1	—
2-1	4.9–5.2	110	1.0	<0.1	1.0	0.6	0.6	<0.1	4.1
		—	—	—	—	—	—	—	—
		—	0.4	65	11	2.0	2.0	0.1	—
		—	0.2	20	<0.1	4.0	5.0	0.1	—
2-2	5.8–6.1	133	<0.05	0.7	<0.1	6.0	7.0	<0.1	13
		—	—	—	—	—	—	—	—
		—	3.8	<0.1	0.1	0.2	0.3	<0.1	—
		—	0.6	<0.1	<0.1	0.9	1.0	<0.1	—
3-1	4.6–4.9	261	1.0	<0.1	1.2	0.6	0.6	<0.1	4.4
		—	—	—	—	—	—	—	—
		—	0.6	52	43	0.2	0.5	<0.1	—
		—	0.5	40	0.2	1.0	2.0	<0.1	—
		172	0.3	10	<0.1	1.5	2.0	<0.1	27

^a identifier indicates upgradient (U) or station (1,2,3) and well number (Figure 1 plan and cross section views). ^b mbls indicates meters below land surface. ^c For each well and constituent, measurements are arranged vertically for the July 2003, November 2003, August 2004, and November 2004 sampling events. ^d "—" indicates not measured.

NP1–2EC, caffeine, paraxanthine, E2, and E1 (Figures 2i–t; Tables 1 and 2) were measured at depths from 4.1–5.2 m (wells 1-1, 1-2, 1-3, and 1-4), where conditions were sub-oxic/anoxic (Table 1, Figure 2e). Lower concentrations of these OWC were observed in the more oxic shallow well (well 1-0; 3.5 m) and in the deepest well (well 1-5; 5.6 m) that is apparently screened below the plume.

The observed vertical concentration patterns suggest that many of the OWC may be preferentially removed in the more oxic portions of the plume relative to the sub-oxic/anoxic portion. In the suboxic/anoxic zone, concentrations of DAS, DSBP, NP1-3EO, NP1EC, E1, and E2 are similar to those measured in the septic tank on the same day (Tables 1 and 2). The similarity of septic tank and groundwater concentrations in the deeper portion of the plume suggests a steady input and limited removal of these OWC over the residence time required to move from the septic tank to the station 1 wells. This travel time is estimated to be approximately 1–2 weeks based on a 2-day engineered system residence time and vadose-zone and groundwater velocities of 0.15–0.3 m/day (35).

Near source concentrations of caffeine and paraxanthine are likewise lowest in the most shallow well (Figure 2q,r). However, unlike the OWC discussed above, concentrations of caffeine and paraxanthine are substantially lower (60-fold or more) than those measured in the septic tank at all station 1 wells (Table 2). Yet, the ratios of caffeine to paraxanthine in the tank (3.0) and the station 1 wells (2.3–2.8) are similar. These observations could indicate that (1) loading of caffeine and paraxanthine to the septic tank changed markedly and in tandem in the prior week(s) to sampling, or (2) substantial removal of both constituents occurred at similar rates in transit between the septic tank and the station 1 wells, with further removal occurring preferentially at the most shallow depths.

In contrast to other OWC, NP and NP2EC are up to 6- and 30-fold greater, respectively, in station 1 wells compared to the septic tank (Table 1), suggesting net production of these constituents, possibly in transit from the tank to station 1, with subsequent preferential loss along the shallowest flow lines. While the greatest NPEC production from higher ethoxylated surfactants would be expected under more oxic

conditions (37) such as existed in well 1-0 in November 2003 (Table 3), NPEC oxidation products have been observed in incubations of NPEOs with anaerobic marine sediments (38). This may also explain the larger NP2EC concentrations measured in deeper suboxic/anoxic wells at station 1 relative to the shallowest well. Overall, the fraction of total NPEC (sum of NP1-2EC) relative to the sum of total NPEO (sum of NP1-3EO, NP, and NP1-2EC) is linearly correlated with more oxic conditions in the plume, represented as DO concentration (positive correlation; $R^2 = 0.77$) and percent $\text{NH}_3\text{-N}$ (negative correlation; $R^2 = 0.58$) for all wells.

The concentrations of OWC measured in the shallowest portion of the plume appear to fluctuate with the changes in oxygenation conditions at that depth. Higher concentrations of OWC were measured in well 1-0 in July 2003 and November 2004 (MBAS only) when DO was lower compared to when DO was higher at that depth in November 2003 (Tables 1 and 2; Figures 2j–t). The observed temporal variations are consistent with greater preservation of OWC under the more reducing conditions that existed in this well in July 2003; however, changes in loading rates may have contributed to these concentration fluctuations. Vertical movement of the plume does not appear to be a factor, as the similarity in profiles for the sum of $\text{NH}_3\text{-N}$ and $\text{NO}_3\text{-N}$ in November 2003, August 2004, and November 2004 (Figure 2a) suggest that the plume is vertically stable over time.

Occurrence of Estrogen Conjugates. The only estrogen conjugate detected in the wells sampled was E1-3S, and it was detected only in wells within the core of the plume, at levels of 1.0–4.0 ng/L (Table 2). The fraction of estrogen conjugates relative to the free estrogens measured on the same date were low (3–5% of the sum of E1 and E2 in samples from wells 2-1 and 3-1, respectively), but the similarity of concentrations measured across the traverse suggests that once in groundwater, E1-3S is readily transported.

Because steroid conjugates are the dominant form of estrogen excreted in urine, it appears that estrogen conjugates were transformed by conversion to the free forms observed in the anaerobic septic tank and groundwater samples before wastewater reached the first set of wells. Recent studies (25, 39) have reported that estrogen glucuronide conjugates entering sewers are de-conjugated before reaching municipal sewage treatment plants, likely due to extracellular hydrolytic glucuronidases released from some bacterial populations, including *E. coli* (39) present in human feces. Release of free estrogens from sulfate conjugates and the presence of corresponding sulfatases has not been clearly documented. Consistent with results from the present study, E1-3S was the primary conjugate found in sewage influent and effluent at other sites (25, 39).

Potential Near-Source Loss Mechanisms for OWC. Microbial transformation or mineral surface catalyzed reactions could account for some of the apparent aqueous depletion occurring along the more oxic flow lines. For example, Lee et al. (41) suggest that clay and oxide surfaces may catalyze abiotic oxidation of E2 to E1, and the transformation of NPEO compounds and linear alkylbenzene sulfonates (LAS), the primary components of MBAS in wastewaters (12), is more rapid under oxic conditions (37, 40). Removal by microbial transformation is consistent with lower MBAS concentrations in well 1-0 in November 2003 (Figure 2j) when conditions were more oxic compared to July 2003 and November 2004, when DO was lower.

It is possible that the wastewater plume and variations in redox chemistry also could affect the aquifer solids in ways that enhance sorption of OWC to sediment organic matter (SOM) and/or mineral surfaces along the more oxic flow lines. For example, greater concomitant sorption of dissolved organic matter (DOM) to solids with increased iron and manganese oxyhydroxide coatings is expected (42), and the

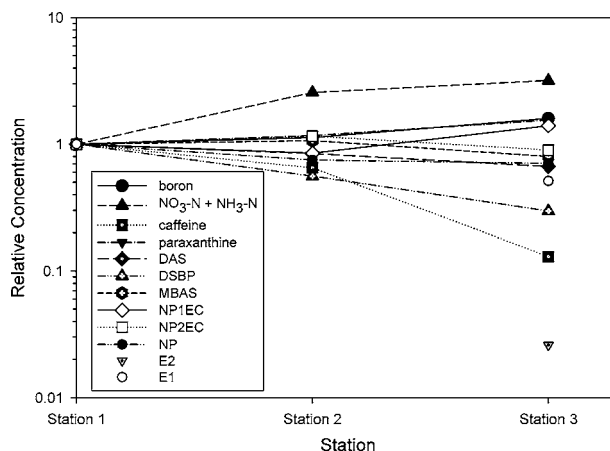


FIGURE 3. November 2003 concentrations of constituents at station 2 (well 2-1) and station 3 (well 3-1) normalized to the average concentration determined for station 1 (wells 1-3 and 1-4), all at a depth range of 4.7–5.2 m. E1 and E2 measurements are not available for well 2-1 in November 2003.

latter have been correlated with the sorption of LAS in soils (43). However, there would need to be a change in surface chemistries that increase, to a similar extent (by tens to several 100-fold), the sorption capacity of all important sorbents (e.g., SOM and oxyhydroxides) in the upper portion of the plume to explain the reduced aqueous concentrations of both the most water-soluble OWC, such as caffeine and paraxanthine (20, 21) and the more hydrophobic OWC, such as NP ($K_{oc} = 10^5$; 44), and E2 and E1 ($K_{oc} = 10^3$; 41). Furthermore, if sorption was reversible, an increase in sorption energy or capacity in the upper portion of the plume would eventually equilibrate under steady-state conditions, and breakthrough for more soluble contaminants at such short distances from the source would be likely. Further monitoring will be required to determine if steady-state conditions prevail at this site.

Longitudinal Behavior of OWC. Many of the OWC and wastewater indicators are still present 6 m (station 3) from the leachate pit at concentrations within a factor of 2 of station 1 and septic tank concentrations (Tables 1 and 2), suggesting little loss of these constituents in transit from the septic system and through the aquifer. Figure 3 shows November 2003 concentrations of measured compounds in the core of the plume at stations 2 and 3 relative to station 1. We observe that concentrations of many OWC, including DAS, NP, NP1EC, NP2EC, MBAS, paraxanthine, and E1 vary by a factor of approximately 2 or less among wells completed to similar depths at the three stations. Assuming that continuous flow lines intersect these three stations at this depth range (4.7–5.2 m, Figure 1), these data suggest (1) relatively steady input of these OWC over the residence time represented by this traverse, and (2) little net losses along these sub-oxic flow lines (Table 3). For NP2EC in particular, the relative uniformity of groundwater concentrations along the traverse (Figure 3), together with the fact that these concentrations are substantially greater than septic tank concentrations (Table 1), may indicate that most NP2EC production occurs somewhere between the septic tank and the station 1 wells, with limited net production subsequently downgradient. Non-steady-state inputs cannot be ruled out though.

The apparent persistence in groundwater of NP1EC and NP2EC over the distance investigated is consistent with a study of APEO behavior in river water infiltrating to groundwater over a distance as far as 14 m (45), although unlike the present study, Ahel et al. (45) measured substantially lower concentrations of the lower homologues (NP1-2EO) and NP over the first several meters of transport in the aquifer.

Differing oxygenation conditions, sorption capacities, and microbial activity may account for these apparent differences in behavior of NP and the lower homologues between these two study sites.

Concentrations of E2 and caffeine are 40-fold and 8-fold less, respectively, at station 3 relative to station 1 (Figure 3, Table 2), suggesting substantial losses of these two constituents along the traverse. E2 appears to be removed without concomitant net production of E1, while caffeine is likely biotransformed to paraxanthine. From station 1 to station 3, the rate of caffeine transformation to paraxanthine in groundwater appears to be approximately $0.07\text{--}0.014\text{ day}^{-1}$ based on linear regression of caffeine concentrations measured in the 4.7–5.2 m depth range at each of the stations (Table 2) versus the residence time, calculated using a groundwater velocity of 0.15–0.3 m/day (35), and assuming conservation of total caffeine and paraxanthine; the sum of these two constituents remains fairly constant among wells 1-3, 1-4, 2-1, and 3-1, even though all groundwater measurements are substantially less than septic tank levels (Table 2). This transformation rate is similar to that reported elsewhere (0.05 day^{-1} ; 21), although Buerge et al. (21) targeted only caffeine and no transformation products for measurement in those elimination experiments.

Longer-term monitoring will be required to more completely inform our understanding of loading dynamics and constrain interpretation of transport behavior in this wastewater plume. The fact that boron, a reportedly conservative wastewater tracer, varies by less than a factor of 2 across the traverse is consistent with the interpretation of a relatively steady loading of laundry input. Note that mineralization of organic nitrogen or an increase in human waste may decouple the behavior of boron from the nitrogen species, as the sum of $\text{NO}_3\text{--N}$ and $\text{NH}_3\text{--N}$ increases 3-fold gradually over the traverse (Figure 3).

Implications for Groundwater Impact. Many OWC exhibited greater apparent losses along shallow flow lines in this wastewater plume, where conditions were more oxic than in the plume core. This suggests that design features of on-site sewage disposal systems that are likely to control the development of subsurface anoxia, such as loading rates, retention times, and depth to water table, may affect the extent to which OWC impact downgradient drinking water supplies and groundwater-fed surface water bodies, particularly in areas with high-densities of septic systems, such as Cape Cod. Note that while the more potent estrogens E2 and E1 appear to be more attenuated with distance, E1 was still present at concentrations (approximately 20 ng/L; Table 2) that approach those reported to induce vitellogenin production in male fish (9).

Near-source concentration profiles of DAS, DSBP, caffeine, and paraxanthine were similar to those of the estrogenic OWC. This suggests that these FWA, caffeine, and paraxanthine, which are typically elevated in wastewater effluent, may have utility as effective indicators of impact from estrogenic OWC to groundwater and surface water, complementing traditional tracers such as boron and inorganic nitrogen species. This is important, because interpreting wastewater impact to groundwater using the latter constituents can be complicated by multiple source types and substantial natural background signals. However, the utility of caffeine, paraxanthine, and FWA in assessing the impact of estrogenic OWC to groundwater will require better understanding of subsurface persistence and mobility of these indicators as well as the estrogenic OWC.

Acknowledgments

This work was primarily supported by grants from Massachusetts Environmental Trust, Dolphin Foundation, the Agua Fund of the Tides Foundation, and Babylon Breast

Cancer Coalition. Additional support came from an EPA STAR grant (no. R-82900701-0) to Bruce Brownawell, but the work has not been subjected to the Agency's required policy review, and therefore, does not necessarily reflect the views of the Agency. We thank Joseph Ruggieri for HPLC–MC analysis of alkylphenols; Philip Gschwend for use of field and lab equipment; and Theresa Kennedy, Kathleen Attfield, and Jessica Schifano for help with sampling. Earlier drafts of the manuscript were greatly improved by suggestions provided by Allison MacKay and Kathy DeJong, and we also thank three anonymous reviewers for their valuable input in improving this manuscript. We are grateful to the Cape Cod family that allowed us to establish this study site on their property, and to Cheryl Osimo for facilitating collaboration with them. Any use of trade, firm, or product names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

Supporting Information Available

Detailed description of analytical methods used for analyses of OWC. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Received for review December 28, 2005. Revised manuscript received May 2, 2006. Accepted June 9, 2006.

ES052595+